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(19)(CA) **CANADIAN PATENT** (12)

# (54) Herbicides

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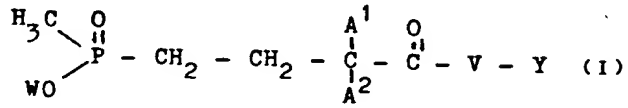
# Herbicides

The present invention relates to herbicides which contain an active ingredient of the formula I,



(I)

in which

$A^1$ denotes H and $A^2$ denotes $NH_2$, or $A^1$ and $A^2$ together denote an oxygen atom,

V denotes O or NH,

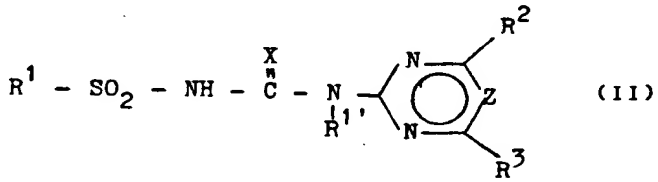
Y, where V = O, denotes hydrogen or $(C_1-C_4)$alkyl, or

Y, where V = NH, denotes a radical of the formula $-CH(CH_3)-CONH-CH(CH_3)-COOH$ or $-CH(CH_3)-CONH-CH[CH_2CH(CH_3)_2]-COOH$, and, irrespective of the meaning of V,

W denotes hydrogen,

or a salt thereof,

in combination with a compound of the formula II



(II)

in which

$R^1$ denotes $(C_1-C_4)$ alkyl, $(C_2-C_6)$ alkenyl, $(C_2-C_6)$ alkynyl, which may in each case be halogenated, $(C_1-C_4)$ alkylamino, di$(C_1-C_4$-alkyl)-amino, [N-$(C_1-C_4$-alkylsulfonyl)-N-$(C_1-C_4$-alkyl)]-amino, where the alkyl radicals may be halogenated, phenyl, benzyl, phenoxy, pyrazolyl or thienyl which may all be substituted by $(C_1-C_4)$ alkyl, $(C_2-C_6)$ alkenyl, $(C_2-C_6)$ alkynyl or $(C_1-C_4)$ alkoxy which may all be substituted by halogen or $(C_1-C_4$-alkoxy)carbonyl,

furthermore by halogen, $CF_3$, nitro or a radical of the formula $-COOR^4$, in which

$R^4$ denotes H, $(C_1-C_4)$ alkyl, $(C_2-C_6)$-alkenyl, $(C_2-C_6)$ alkynyl, $(C_1-C_4)$ alkoxy-$(C_1-C_4)$ alkyl or halo $(C_1-C_4)$ alkyl,

furthermore by a radical of the formula $-S(O)_nR^5$, in which

$R^5$ denotes $(C_1-C_4)$ alkyl, $(C_1-C_4)$ alkoxy, halo $(C_1-C_4)$ alkyl, $(C_1-C_4)$ alkoxy-$(C_1-C_4)$ alkyl, $(C_1-C_4)$ alkoxy-carbonyl-$(C_1-C_4)$ alkyl, di$(C_1-C_4$-alkyl)-amino, $(C_1-C_4)$ alkylamino, $(C_1-C_4)$ alkoxy-$(C_1-C_4)$alkylamino, and n denotes 0, 1 or 2,

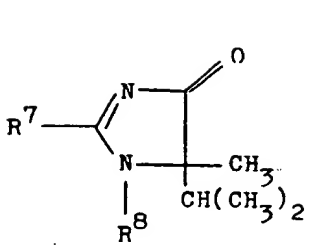
$R^{1'}$ denotes H, $(C_1-C_4)$alkyl or $(C_2-C_4)$alkenyl,

$R^2$ and $R^3$, independently of one another, denote $(C_1-C_4)$-alkyl or $(C_1-C_4)$ alkoxy which are both optionally monosubstituted or polysubstituted by halogen, $(C_1-C_4)$ alkoxy or $(C_1-C_4$-alkoxy)-carbonyl, $(C_2-C_6)$ alkenyl, $(C_2-C_6)$ alkynyl, $(C_2-C_6)$ alkenyloxy, $(C_2-C_6)$ alkynyloxy or halogen,

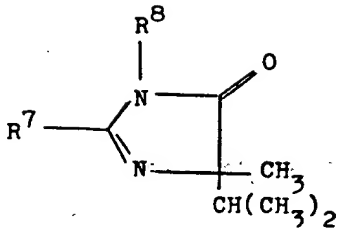
X denotes O, S or $NR^6$, where $R^6$ = $(C_1-C_4)$ alkyl or $(C_1-C_4)$ alkoxy, and

Z denotes CH or N, or a salt thereof,

or with a compound of the formula III or III', or salts thereof,



(III)



(III')

in which

$R^7$ denotes phenyl, pyridyl, and quinolyl which are all optionally monosubstituted or polysubstituted by $(C_1-C_4)$ alkyl or $(C_1-C_4)$ alkoxy, which may both be monosubstituted or polysubstituted by halogen, are further substituted by a radical of the formula $-COOR^9$, $-COO-CH_2R^9-COOR^9$,

$-CH_2R^9-COO(C_1-C_4\text{-alkyl})$ or $CH_2R^9-COOCH_2R^9-COOR^9$,

in which, in each case independently of one another, $R^9$ denotes H or $(C_1-C_4)$ alkyl, or a radical of the formula $-CH_2-S(O)_n-(C_1-C_4)$-alkyl, where n denotes 0, 1 or 2, and

$R^8$ denotes H or a radical of the formula $-CONH(C_1-C_4$-alkyl), $-OCO(C_1-C_4$-alkyl) or $-CO(C_1-C_4$-alkyl).

In the case where $R^8$ = H, the two formulae III and III' exist in tautomeric equilibrium. Depending on the radical $R^8$ and the other substituents, the one or the other form (III or III') can therefore be present, see German Offenlegungsschrift 3,121,636 and German Offenlegungsschrift 2,833,274.

The compounds of the formula I where V = O are described in U.S. Patent 4,168,936 and European Patent 30,424, whereas the compounds of the formula I where V = NH are known from U.S. Patent 4,309,208, S. Omura et al., The

Japanese Journal of Antibiotics, Volume XXXVIII-2, p. 542 (1985); and H.S. Seto et al., The Journal of Antibiotics, Vol. XXXVI-1, pp. 96 - 98 (1983). Of the compounds of the formula I, preferred compounds are

Ia: $A^1$ = H, $A^2$ = $NH_2$; V - Y = OH, W = H, and the salts thereof; monoammonium salt; common name: glufosinate-ammonium.

Ib: $A^1$ and $A^2$ together = oxygen; V - Y = OH, W = H, and the salts thereof.

Ic: $A^1$ = H, $A^2$ = $NH_2$; V = NH; Y = $-CH(CH_3)-CONH-CH(CH_3)COOH$, W = H, and the salts thereof; common name: bialaphos.

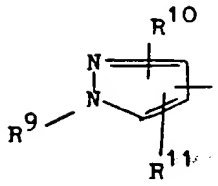
Id: $A^1$ = H, $A^2$ = $NH_2$; V = NH; Y = $-CH(CH_3)-CONH-CH(CH_2CH-(CH_3)_2)COOH$, W = H, and the salts thereof; common name: phosalacine (S. Omura et al. The Japanese Journal of Antibiotics, 37 (2), p. 542 (1985)).

Preferred compounds of the formula II are:

Type 1: Alkylaminosulfonylureas of the abovementioned formula II, in which

$R^1$ denotes [N-($C_1$-$C_4$-alkylsulfonyl)-N-($C_1$-$C_4$-alkyl)amino], where the alkyl radicals may in each case be halogenated, and X denotes O, see EP-A 131,258; of these, the compound IIa in which $R^1$ denotes $(CH_3SO_2)-(CH_3)N-$, $R^2$ and $R^3$ denote $OCH_3$, and Z denotes CH are of particular importance.

Type 2: Pyrazolylsulfonylureas of the abovementioned formula II in which $R^1$ denotes a radical of the formula



in which

$R^9$ has the abovementioned meaning,

$R^{10}$ denotes H, ($C_1$-$C_4$) alkyl, ($C_1$-$C_4$) alkoxy, or a radical of the formula $-COOR^4$ or $-S(O)_nR^{5'}$, in which $R^{5'}$ = ($C_1$-$C_4$) alkyl, ($C_1$-$C_4$) alkoxy, halo ($C_1$-$C_4$) alkyl, ($C_1$-$C_4$) alkylamino or di($C_1$-$C_4$-alkyl)amino, and

$R^{11}$ denotes H, halogen, ($C_1$-$C_4$) alkyl or ($C_1$-$C_4$) alkoxy, which may both be halogenated, and X denotes O, see EP-A 87,780.

Of these compounds, the following are particularly suitable according to the invention:

Compound IIb: $R^{1'}$ = H, $R^1$ = 1,3,5-trimethyl-pyrazol-4-yl, X = O, $R^2$ = $CH_3$, $R^3$ = $OCH_3$ andZ = N.

IIc: $R^{1'}$ = H, $R^1$ = 1,3,5-trimethyl-pyrazol-4-yl, X = O, $R^2$ = $CH_3$, $R^3$ = $OCH_3$ and Z = CH.

IId: $R^{1'}$ = H, $R^1$ = 1,3,5-trimethyl-pyrazol-4-yl, X = O, $R^2$ = $R^3$ = $CH_3$ and Z = CH.

IIe: $R^{1'}$ = H, $R^1$ = 5-chloro-1,3-dimethyl-pyrazol-4-yl, X = O, $R^2$ = $CH_3$, $R^3$ = $OCH_3$ and Z = N.

IIf: $R^{1'}$ = H, $R^1$ = 5-chloro-1,3-dimethyl-pyrazol-4-yl, X = O, $R^2$ = $CH_3$, $R^3$ = $OCH_3$ and Z = CH.

IIg: $R^{1'}$ = H, $R^1$ = 5-chloro-1,3-dimethyl-pyrazol-4-yl, X = O, $R^2$ = $R^3$ = $CH_3$ and Z = CH.

IIh: $R^{1'}$ = H, $R^1$ = 1,5-dimethyl-pyrazol-4-yl, X = O, $R^2$ = $R^3$ = $OCH_3$ and Z = CH.

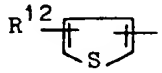
IIi: $R^{1'}$ = H, $R^1$ = 1,3-dimethyl-5-difluoromethoxy-pyrazol-4-yl, X = O, $R^2$ = $CH_3$, $R^3$ = $OCH_3$ and Z = H.

IIk: $R^{1'}$ = H, $R^1$ = 4-ethoxycarbonyl-1-methyl-pyrazol-5-yl, X = O, $R^2$ = $R^3$ = $CH_3$ and Z = CH.

II(l): $R^{1'}$ = H, $R^1$ = 4-ethoxycarbonyl-1-methyl-pyrazol-5-yl, X = O, $R^2$ = $R^3$ = $OCH_3$ and Z = CH.

Type 3: Thienylsulfonylureas of the abovementioned formula II, in which

$R^1$ denotes a radical of the formula



in which
$R^{12}$ denotes H, halogen, ($C_1$-$C_4$) alkyl, ($C_2$-$C_4$) alkenyl or ($C_1$-$C_4$) alkoxy, where all three of the lastmentioned radicals may be halogenated, a radical of the formula $-COOR^{4'}$ where $R^{4'}$ = H, ($C_1$-$C_4$) alkyl or ($C_2$-$C_6$)alkenyl, or a radical of the formula $-S(O)_n-R^{5'}$, and X denotes O, see U.S. Patent 4,431,029, JP-A 60/197,676, JP-A 60/139,691 and JP-A 60/193,983.

Of these compounds, examples which may be mentioned are the compounds
IIm : $R^1$ = 2-methoxycarbonyl-3-thienyl, $R^{1'}$ = H, X = O, $R^2$ = $OCH_3$, $R^3$ = $CH_3$ and Z = N (thiameturon-methyl)

IIn: $R^1$ = 3-(pentafluoro-1-propenyl)-2-thienyl, $R^{1'}$ = H, X = O, $R^2$ and $R^3$ = $OCH_3$, Z = N or CH

IIo: $R^1$ = 3-(2-chloro-1,2-difluoroethenyl)-2-

thienyl, $R^{1'}$ = H, X = O, $R^2$ and $R^3$ = $OCH_3$ and Z = N or CH

IIp: $R^1$ = 3-(2-chloro-1,2-difluoroethenyl)-2-thienyl, $R^{1'}$ = H, X = O, $R^2$ = $CH_3$, $R^3$ = $OCH_3$ and Z = N or CH

IIq: $R^1$ = 3-(pentafluoro-1-propenyl)-2-thienyl, $R^{1'}$ = H, X = O, $R^2$ = $CH_3$, $R^3$ = $OCH_3$ and Z = N or CH

Type 4: Phenyl-, phenoxy- and benzylsulfonylureas of the formula II, in which

$R^1$ denotes phenyl, phenoxy or benzyl which may both be substituted by halogen, ($C_1$-$C_4$) alkyl or ($C_1$-$C_4$) alkoxy which may both be halogenated, or a radical of the formula $-COOR^4$ or $-S(O)_nR^{5'}$, and
X denotes O, see EP-A 51,466, EP-A 113,956, EP-A 7,687 and U.S. Patent 4,514,212.

Amongst these, the following compounds may be mentioned as examples:

IIs: $R^{1'}$ = H, $R^1$ = 2-ethoxycarbonyl-phenyl, X = O, $R^2$ = Cl, $R^3$ = $OCH_3$ and Z = CH

IIt: $R^{1'}$ = H, $R^1$ = 2-methoxycarbonyl-phenyl-methyl, X = O, $R^2$ = $R^3$ = $OCH_3$ and Z = CH.

IIu: $R^{1'}$ = H, $R^1$ = 2-methoxycarbonyl-phenyl, X = O, $R^2$ and $R^3$ = $CH_3$ and Z = CH; common name: sulfometuron-methyl

IIv: $R^{1'}$ = $CH_3$, $R^1$ = 2-methoxycarbonyl-phenyl, X = O, $R^2$ = $CH_3$, $R^3$ = $OCH_3$ and Z = N

IIw: $R^{1'}$ = H, $R^1$ = 2-methoxycarbonyl-phenyl, X = O, $R^2$ = $CH_3$, $R^3$ = $OCH_3$ and Z = N (metsulfuron-methyl)

IIx: $R^{1'}$ = H, $R^1$ = 2-(2-chloroethoxy)-phenyl, X = O, $R^2$ = $CH_3$, $R^3$ = $OCH_3$ and Z = N

IIy: $R^{1'}$ = H, $R^1$ = 2-chlorophenyl, X = O, $R^2$ = $CH_3$, $R^3$ = $OCH_3$ and Z = N (chlorsulfuron).

Compounds which may be mentioned as being preferred amongst the compounds of the formula III or III' are those in which

$R^7$ = pyridyl which may be substituted by $(C_1-C_4)$-alkyl, or a radical of the formula $-COOR^9$, $-COOCH_2R^9-COOR^9$, $-CH_2R^9-COO(C_1-C_4\text{-alkyl})$, $-CH_2(R^9)-COOCH_2R^9-COOR^9$ or $-CH_2-S(O)_n-(C_1-C_4\text{-alkyl})$, and

$R^8$ has the abovementioned meaning.
(see Japanese Offenlegungsschrift 59/225,180, EP-A 133,311 and EP-A 41,624).

Of these compounds III and III', compounds which may be mentioned as examples are

IIIa: $R^7$ = 3-methoxycarbonyl-2-pyridyl and $R^8$ = methylaminocarbonyl.

IIIb: $R^7$ = 3-methoxycarbonyl-2-pyridyl and $R^8$ = ethylaminocarbonyl.

IIIc: $R^7$ = 3-methoxycarbonyl-2-pyridyl and $R^8$ = methoxycarbonyl.

IIId: $R^7$ = 3-carboxy-2-pyridyl and $R^8$ = H; the isopropylammonium salt has the common name: imazapir.

Amongst the compounds of the formulae III and III', the

following compound is furthermore of particular importance:

IIIe: $R^7$ = 2-methoxycarbonyl-5-methyl-phenyl and $R^8$ = H

The combinations according to the invention also cover the salts of the compounds of the formulae I to III which can be employed for agriculture.

Suitable as such are, for example, the conventional alkali metal salts, alkaline-earth metal salts, substituted or unsubstituted ammonium salts, phosphonium salts or sulfonium salts. Amongst the alkaline-earth metal salts and alkali metal salts, the Na, K, Mg or Ca salts are to be mentioned primarily.

Furthermore, the compounds of the formula I can also form acid-addition salts with inorganic acids, such as HCl, HBr, $H_2SO_4$ or $H_3PO_4$, or with organic acids, such as ($C_1$-$C_4$) carboxylic acids, chlorinated acetic acids, tartaric acid or citric acid; these are likewise covered by the invention.

Furthermore, formula I and formula III or III' also cover all corresponding stereoisomers and the mixtures thereof, so that these likewise come under the combinations according to the invention.

The present invention also relates to three-component combinations of compounds of the general formula I with two different active ingredients of the general formula II or III.

The herbicidal active ingredient combinations mentioned exhibit a surprisingly high activity which is greater than could have been expected as a result of the actions of the individual components.

The active ingredient combinations according to the

invention cover a broad range of weeds. They are suitable, for example, for combating annual and perennial weeds, such as, for example, Agropyron, Paspalum, Cynodon, Imperata, Pennisetum, Convolvulus, Cirsium, Rumex and others.

The combinations according to the invention can be employed for selective combating of harmful plants in plantation crops, such as oil palm, coconut palm, rubber tree, citrus fruit, pineapple, cotton, coffee, cocoa inter alia, and also in fruit growing and viticulture. Likewise, the combinations according to the invention can be employed in arable farming in the so-called "no till" or "zero till" methods. However, they can also be used non-selectively on paths, squares, industrial works etc. in order to keep these areas free of undesired vegetative growth.

The ratios of the compounds of the formula I to the compounds of the formula II or III in the mixtures can vary within broad limits, in particular between about 500:1 to 1:10. The choice of mixture ratio depends on various parameters, such as the type of mixture partners, stage of development of the weeds and the range of weeds. Mixture ratios from 100:1 to 1:5 are preferably selected.

The combinations according to the invention can be present both in the form of mixed formulations - wettable powders, emulsion concentrates - which are then used in a conventional fashion diluted with water; however, they can also be prepared as so-called tank mixes by common dilution of the separately formulated components with water.

The application rates of the herbicide of the formula I in the active ingredient mixtures generally vary between 0.25 and 4.0 kg/ha, whereas the application rates of the compounds of the formula II or III can be in the range between 0.01 and 5.0 kg/ha, specifically for

| | | | |
|---|---|---|---|
| Compounds of the formula II, | | between 0.01 and | 2.0 kg of a.i./ha |
| " | type 1 | " 0.01 and | 1.0 kg of a.i./ha |
| " | type 2 | " 0.01 and | 0.5 kg of a.i./ha |
| " | type 3 | " 0.01 and | 0.5 kg of a.i./ha |
| " | type 4 | " 0.05 and | 2.0 kg of a.i./ha |
| and | | | |
| compounds of the formula III | | " 0.05 and | 2.0 kg of a.i./ha |

The agents according to the invention can be marketed in the conventional formulations which are known to those skilled in the art, for example as wettable powders, dusting agents, granules, dispersion concentrates, emulsifiable concentrates or sprayable solutions. In this case, the formulated agents generally contain the active ingredient in concentrations from 2 to 95% by weight.

Wettable powders are preparations, uniformly dispersible in water, which contain, besides the active ingredient and in addition to a diluent or inert material, wetting agents, for example polyoxyethylated alkylphenols, polyoxyethylated oleylamines or stearylamines, alkylsulfonates or alkylphenyl sulfonates, and dispersing agents, for example sodium ligninsulfonate, sodium dinaphthylmethanesulfonate or also sodium oleylmethyltaurinate.

Emulsifiable concentrates are obtained by dissolving the active ingredient mixture in an organic solvent, for example butanol, cyclohexanone, dimethylformamide, xylene or alternatively higher-boiling aromatics, and adding a nonionic wetting agent, for example a polyoxyethylated alkylphenol or a polyoxyethylated oleylamine or stearylamine.

In wettable powders, the total concentration of active ingredient is between about 10% and 95%, and the rest comprises the abovementioned formulation additives. In the case of emulsifiable concentrates, the active ingredient concentration is about 10% to 80%. Dust-like formulations usually contain 5% to 20% of active ingredients, sprayable solutions about 2% to 20%. In the case of granules, the active ingredient content depends partly on the form (liquid or solid) in which the active ingredients are present and on which granulation auxiliaries, fillers etc. are used.

For use, the commercially available concentrates are, if appropriate, diluted in a conventional fashion, for example using water in the case of wettable powders and emulsifiable concentrates.

Dust-like and granulated formulations and sprayable solutions are not diluted with further inert substances before use.

A. Formulation Examples

a) The dusting agent is obtained by mixing 10 parts by weight of active ingredient mixture and 90 parts by weight of talc as inert material, and comminuting in a hammer mill.

b) The wettable powder which is easily dispersible in water is obtained by mixing 25 parts by weight of active ingredient mixture, 64 parts by weight of kaolin-containing quartz as inert material, 10 parts by weight of potassium ligninsulfonate and 1 part by weight of sodium oleoylmethyltaurinate as wetting and dispersing agent, and grinding in a pin disc mill.

c) The dispersion concentrate which is easily dispersible in water is prepared by mixing 20 parts by weight of active ingredient mixture with 6 parts by

weight of alkylphenol polyglycol ether (®Triton X 207), 3 parts by weight of isotridecanol polyglycol ether (8 EO) and 71 parts by weight of paraffinic mineral oil (boiling range, for example about 255 to above 377°C), and grinding in a ball mill to a fineness of below 5 microns.

d) An emulsifiable concentrate is obtained from 15 parts by weight of active ingredient mixture, 75 parts by weight of cyclohexanone as solvent and 10 parts by weight of oxyethylated nonylphenol (10 EO) as emulsifier.

B. Biological Examples

Synergism is detected in the following examples by comparing the additive degree of action calculated from the actions of individual components with the experimentally found degree of action of the active ingredient combinations. The additive degree of action is calculated according to the formula of S.R. Colby (cf. Calculating synergistic and antagonistic responses of herbicide combinations, Weeds, 15, 1967, pp. 20 to 22).

This formula is:

$$E = X + Y - \frac{X \cdot Y}{100}$$

where

X denotes the % damage by herbicide A at an application rate of x kg/ha,

Y denotes the % damage by herbicide B at an application rate of y kg/ha,

E denotes the expected % damage by herbicides A + B at an application rate of x + y kg/ha.

If the actual damage is greater than that calculated, the

action of the active ingredient combination is more than additive, i.e. there is a synergistic effect.

Example 1

Seeds of various weed grasses and weeds were sown in sandy loam in plastic pots (Ø 9 cm) and raised for 3 - 4 weeks in a greenhouse under good growth conditions. The compounds of the formula I, formulated as aqueous solutions, water-dispersible powders or emulsion concentrates, and the combination partners were subsequently sprayed, alone and in combination, in the form of sprayable solutions onto the above-ground parts of the plants. The amount of water used in this corresponded to 400 l/ha.

After standing for about 3 weeks in the greenhouse under ideal growth conditions, the herbicidal action was assessed visually. The results are reproduced in Table 1 below.

Table 1:

Herbicidal action of the mixtures according to the invention under greenhouse conditions (according to Example 1)

| Product | Dosage, kg of a.i./ha | % action ECG | PMI |
|---|---|---|---|
| Ia | 0.125 | 10 | 65 |
| | 0.060 | 0 | 30 |
| IIu | 0.008 | 30 | 55 |
| Ia + IIu | 0.125 + 0.008 | 90 (37) | 95 (84) |
| | 0.060 + 0.008 | 75 (30) | 80 (68) |

Abbreviations:

ECG = Echinochloa crus-galli
PMI = Panicum miliaceum
a.i. = active ingredient
Ia = glufosinate

IIa = sulfometuron-methyl
( ) = expected value according to Colby

The results show that an unexpectedly high herbicidal activity which is considerably better than could have been expected as a result of the sum of the individual actions of the active ingredients was achieved using the active ingredient combination.

Example 2

In a field experiment under tropical conditions, the preparations glufosinate-ammonium (Ia) and imazapyr (IIId) were tested alone and in combination in a crop of the gramineae Imperata cylindrica. At the time of application, this species of gramineae had a growth height of 80 to 120 cm; the inflorescence had already formed. The experimental area was not shaded by trees. A standard knapsack sprayer was used for the treatment; the experimental plots had an area of 16 $m^2$.

Each treatment was repeated three times. Evaluation was carried out by visual estimation of the damage.

The results are shown in Table 2 below, the actions having been determined as average values for the damage (in %) from three experiments in each case. The values in parentheses represent the values to be expected according to the Colby formula.

It can be seen from the results that Ia on its own achieved an average to good initial action at the dosages tested; however, the action of Ia fell off in the course of 12 to 20 weeks since resprouting occurs from the below-ground rhizomes. In contrast, herbicide IIId has a weak initial action, and the action was not completely satisfactory even 12 weeks after application.

For combined use of Ia and IIId, where the low and

average dosages for both products were used, it became apparent that both the initial and the long-term action were considerably better than for the individual components; they were markedly greater than the actions calculated according to the Colby formula. Synergism is therefore present.

Table 2:

Action on Imperata cylindrica

| Product | Dosage, kg of a.i./ha | % action after .. days 28 | 84 | 140 (d) |
|---|---|---|---|---|
| Ia | 1.5 | 53 | 34 | 13 |
| | 2.0 | 82 | 39 | 15 |
| | 3.0 | 89 | 62 | 54 |
| IIId | 0.25 | 5 | 35 | 40 |
| | 0.375 | 7 | 50 | 55 |
| | 0.5 | 14 | 72 | 76 |
| Ia + IIId | 1.5 + 0.25 | 68 (55.35) | 93 (57.1) | 74 (47.8) |
| | 1.5 + 0.375 | 83 (56.29) | 97 (67.1) | 87 (60.85) |
| | 2,0 + 0.25 | 85 (82.9) | 98 (60.35) | 82 (49.0) |
| | 2.0 + 0.375 | 88 (83.26) | 98 (69.5) | 89 (69.75) |

a.i. = active ingredient
Ia = glufosinate-ammonium
IIId = imazapir
d = days

Example 3

Under field conditions, a crop of various annual and perennial weeds having a growth height of 5 to 15 cm was divided into plots of 8 $m^2$.

These plots were then treated with the mixtures according to the invention and with the individual components forming these mixtures on their own at various application rates using the post-emergence method. The amount of water applied here was 400 l/ha. After 30 days, the plant damage compared to untreated experimental samples was assessed visually.

The activities of the mixtures and of the individual components against the various weeds are collated in Table 3.

The experimental results shown clearly prove the synergistic actions of the mixtures according to the invention compared to the activities of the individual components. This synergism can be seen particularly clearly on perennial weeds which are difficult to combat, such as, for example, Agropyron or Cirsium.

Table 3:

| Product | Dosage, kg of a.i./ha | % action AGR | SIA | CAR |
|---|---|---|---|---|
| Ia | 0.5 | 0 | 0 | 40 |
| | 1.0 | 27 | 55 | 55 |
| IIu | 0.0125 | 23 | 70 | 0 |
| Ia + IIu | 0.5 + 0.0125 | 63 (23) | 80 (70) | 65 (40) |
| | 1.0 + 0.0125 | 68 (43) | 92 (86) | 85 (55) |

Abbreviations:

AGR = Agropyron repens
SIA = Sinapis arvensis
CAR = Cirsium arvense
a.i. = active ingredient

Example 4

Plants of Commelina communis and Amaranthus retroflexus

were raised analogously to Example 1 in pots (Ø 10 cm) and, at a growth height of about 25 cm, treated with the mixtures according to the invention and the individual components on their own with a water application rate of 1,000 l/ha.

Evaluation by means of visual assessment occurred after about 3 weeks.

The results of this experiment are collated in Table 4. As the data illustrated clearly show, the mixtures of glufosinate-ammonium and various sulfonylurea derivatives exhibit clearly synergistic actions, since in all cases the degrees of action of the mixtures are considerably greater than the values calculated according to Colby for additive effects.

Table 4:

| Product | Dosage kg a.i./ha | % action COMCO | AMARE |
|---|---|---|---|
| Ia | 0,4 | 40 | 5 |
| IIu | 0,1 | 0 | 5 |
| | 0,05 | 0 | 5 |
| | 0,1 | 0 | 5 |
| | 0,5 | 0 | 10 |
| IIy | 0,01 | 0 | 5 |
| IIm | 0,01 | - | 12 |
| | 0,05 | - | 10 |
| | 0,1 | - | 10 |
| | 0,5 | - | 10 |
| IIw | 0,01 | - | 5 |
| | 0,05 | - | 5 |
| | 0,1 | - | 5 |
| | 0,5 | - | 5 |
| Ia + IIu | 0,4 + 0,01 | - | 86 (10) |
| | 0,4 + 0,05 | 73 (40) | 92 (10) |
| | 0,4 + 0,1 | 63 (40) | 99 (10) |
| | 0,4 + 0,5 | 90 (40) | 99 (15) |
| Ia + IIy | 0,4 + 0,01 | 60 (40) | 95 (10) |
| Ia + IIm | 0,4 + 0,01 | - | 85 (16) |
| | 0,4 + 0,05 | - | 83 (15) |
| | 0,4 + 0,1 | - | 88 (15) |
| | 0,4 + 0,5 | - | 88 (15) |
| Ia + IIw | 0,4 + 0,01 | - | 80 (10) |
| | 0,4 + 0,05 | - | 80 (10) |
| | 0,4 + 0,1 | - | 80 (10) |
| | 0,4 + 0,5 | - | 85 (10) |

Abbreviations:

COMCO = Commelina communis
AMARE = Amaranthus retroflexus
a.i. = active ingredient

( ) = expected values according to Colby

Ia = glufosinate-ammonium

IIm = Thiameturon-methyl

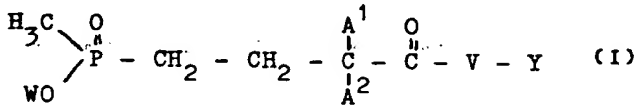
IIu = sulfometuron-methyl

IIw = metsulfuron-methyl

IIy = chlorsulfuron

Patent Claims:

1. A herbicidal composition comprising an active ingredient of the formula I



(I)

in which

$A^1$ denotes H and $A^2$ denotes $NH_2$, or $A^1$ and $A^2$ together denote an oxygen atom,

V denotes O or NH,

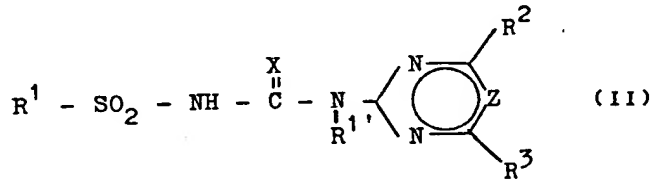
Y, where V = O, denotes hydrogen or $(C_1-C_4)$alkyl, or

Y, where V = NH, denotes a radical of the formula $-CH(CH_3)-CONH-CH(CH_3)-COOH$ or $-CH(CH_3)-CONH-CH[CH_2CH(CH_3)_2]-COOH$, and, irrespective of the meaning of V,

W denotes hydrogen,

or a salt thereof,

in combination with a compound of the formula II



(II)

in which

$R^1$ denotes $(C_1-C_4)$ alkyl, $(C_2-C_6)$ alkenyl, $(C_2-C_6)$ alkynyl, which may in each case be halogenated, $(C_1-C_4)$ alkylamino, di$(C_1-C_4$-alkyl)-amino, [N-$(C_1-C_4$-alkylsulfonyl)-N-$(C_1-C_4$-alkyl)]-amino, where the alkyl radicals may be halogenated, phenyl, benzyl, phenoxy, pyrazolyl or thienyl which may all be substituted by $(C_1-C_4)$ alkyl, $(C_2-C_6)$ alkenyl, $(C_2-C_6)$ alkynyl or $(C_1-C_4)$ alkoxy which may all be substituted by halogen or $(C_1-C_4$-alkoxy)carbonyl,

furthermore by halogen, $CF_3$, nitro or a radical of the formula $-COOR^4$, in which

$R^4$ denotes H, $(C_1-C_4)$ alkyl,

($C_2$-$C_6$) alkenyl, ($C_2$-$C_6$) alkynyl, ($C_1$-$C_4$) alkoxy-($C_1$-$C_4$) alkyl or halo ($C_1$-$C_4$) alkyl,

furthermore by a radical of the formula $-S(O)_nR^5$, in which

$R^5$ denotes ($C_1$-$C_4$) alkyl, ($C_1$-$C_4$) alkoxy, halo ($C_1$-$C_4$) alkyl, ($C_1$-$C_4$) alkoxy-($C_1$-$C_4$) alkyl, ($C_1$-$C_4$) alkoxy-carbonyl-($C_1$-$C_4$) alkyl, di($C_1$-$C_4$-alkyl)-amino, ($C_1$-$C_4$) alkylamino, ($C_1$-$C_4$) alkoxy-($C_1$-$C_4$)alkylamino, and n denotes 0, 1 or 2,

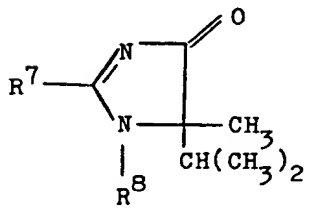
$R^{1'}$ denotes H, ($C_1$-$C_4$)alkyl or ($C_2$-$C_4$)alkenyl,

$R^2$ and $R^3$, independently of one another, denote ($C_1$-$C_4$)-alkyl or ($C_1$-$C_4$) alkoxy which are both optionally monosubstituted or polysubstituted by halogen, ($C_1$-$C_4$) alkoxy or ($C_1$-$C_4$-alkoxy)-carbonyl, ($C_2$-$C_6$) alkenyl, ($C_2$-$C_6$) alkynyl, ($C_2$-$C_6$) alkenyloxy, ($C_2$-$C_6$) alkynyloxy or halogen,

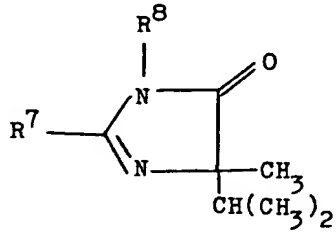
X denotes O, S or $NR^6$, where $R^6$ = ($C_1$-$C_4$) alkyl or ($C_1$-$C_4$) alkoxy, and

Z denotes CH or N, or a salt thereof,

or with a compound of the formula III or III', or salts thereof,



(III)



(III')

in which

$R^7$ denotes phenyl, pyridyl, and quinolyl which are all optionally monosubstituted or polysubstituted by ($C_1$-$C_4$) alkyl or ($C_1$-$C_4$) alkoxy, which may both be monosubstituted or polysubstituted by halogen, are further substituted by a radical of the formula $-COOR^9$, $-COO-CH_2R^9-COOR^9$,

$-CH_2R^9-COO(C_1-C_4\text{-alkyl})$ or $CH_2R^9-COOCH_2R^9-COOR^9$,

in which, in each case independently of one another, $R^9$ denotes H or ($C_1$-$C_4$) alkyl, or a radical of the formula $-CH_2-S(O)_n-(C_1-C_4)$-alkyl, where n denotes 0, 1 or 2, and

$R^8$ denotes H or a radical of the formula $-CONH(C_1-C_4$-alkyl), $-OCO(C_1-C_4$-alkyl) or $-CO(C_1-C_4$-alkyl).

2. A herbicidal composition as claimed in claim 1, comprising an active ingredient of the formula I, in which $A^1$ denotes H, $A^2$ denotes $NH_2$ and V, Y and W have the meanings of claim 1, or the salts thereof, in combination with a compound of the formula II, where, in the formula II, $R^1$ denotes ($C_1$-$C_4$) alkoxycarbonyl-thienyl, ($C_1$-$C_4$) alkoxycarbonylphenyl or chlorophenyl, $R^{1'}$ denotes H or $CH_3$, $R^2$ and $R^3$ denote ($C_1$-$C_4$) alkyl or ($C_1$-$C_4$) alkoxy, X denotes O and Z denotes N or CH.

3. A herbicidal composition, as claimed in claim 1, comprising a compound of the formula I, in which $A^1$ denotes H, $A^2$ denotes $NH_2$, V-Y denotes OH and W denotes H, or the salt thereof; in combination with a compound of the formula II, in which $R^1$ denotes 2-methoxycarbonyl-3-thienyl, 2-methoxycarbonylphenyl or 2-chlorophenyl; $R^{1'}$ denotes H; $R^2$ and $R^3$ denote $OCH_3$ or $CH_3$, X denotes O and

Z denotes N or CH.

4. A herbicidal composition as claimed in claim 1, comprising, besides the compound of the formula I, a compound of the formula III or III', or a salt thereof, where, in the formula III or III', $R^7$ denotes carboxypyridyl or ($C_1$-$C_4$-alkoxy)-carbonyl-pyridyl and $R^8$ denotes H or -CONH($C_1$-$C_4$)-alkyl.

5. A herbicidal composition as claimed in any one of claims 1 to 4, wherein the ratio of the compounds of the formula I to the compounds of the formula II or III varies in the range between 500:1 to 1:10.

6. A herbicidal composition as claimed in any one of claims 1 to 4, wherein the ratio of the compounds of the formula I to the compounds of the formula II or III varies in the range between 100:1 and 1:5.

7. A process for combating harmful plants, wherein a herbicidal composition as claimed in any one of claims 1 to 4 is applied to the plants or to a cultivated area containing the plants in an effective amount.

8. A process for combating harmful plants, wherein a herbicidal composition as claimed in claim 5 is applied to the plants or to a cultivated area containing the plants in an effective amount.

9. The use of a herbicidal composition as claimed in any one of claims 1 to 4 for combating harmful plants.

10. The use of a herbicidal composition as claimed in claim 5 for combating harmful plants.

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